

Microscopic properties of the “pinwheel” kagome compound $\text{Rb}_2\text{Cu}_3\text{SnF}_{12}$

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By $^{63,65}\text{Cu}$ nuclear magnetic resonance (NMR) in magnetic field up to 30 T we study the microscopic properties of the 12-site “pinwheel” valence bond solid state in $\text{Rb}_2\text{Cu}_3\text{SnF}_{12}$. We find evidence of a strong transverse staggered spin polarization existing in the ground state. The temperature and field dependence of the local hyperfine fields, i.e. the spin polarizations, points to a strong anisotropy of the exchange interactions. This is furthermore corroborated by the field dependence of the singlet-triplet gap $\Delta(H)$, which does not close at some critical field, but is only lowered to a large residual value $\approx \Delta(0)/2$, and rises again at higher fields. No evidence of a phase transition was detected down to 1.5 K.

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Frustrated magnetic systems attract a lot of interest as the interplay of frustration and quantum effects in them bring about the emergence of many exotic ground states [1, 2]. The ($S=1/2$) kagome Heisenberg lattice has a particularly high level of frustration leading to a nonmagnetic ground state. It is well established that a large number of singlet states, the number growing exponentially with the size of the system, is lying below the triplet states within a spin gap $\Delta \sim J/20$ (where J is the strength of the antiferromagnetic coupling) [3]. However, despite many theoretical efforts, the nature of the ground state remains an open question. There have been different proposals for the ground state, including various quantum spin liquids [4–7] with unbroken lattice symmetry and valence bond solids (VBS) [8–10] where the lattice symmetry is broken. Unfortunately, only a handful of real systems do not magnetically order at low temperatures, and not all are well suited to study the properties of their ground states. Even fewer of them can be grown as single crystals and without intrinsic disorder which complicates the interpretation of experimental results.

Recently, a singlet ground state has been found in a distorted kagome system $\text{Rb}_2\text{Cu}_3\text{SnF}_{12}$ [11], where the $S=1/2$ spin is carried by the copper Cu^{2+} ion enclosed in an F_6 octahedron. The distortion of the kagome lattice can be seen as 6 elongated hexagons surrounding a regular one, and the spins are connected through the $\text{Cu}^{2+}-\text{F}^--\text{Cu}^{2+}$ bonds with 4 different bonding angles, creating 4 different exchange couplings. Magnetization measurements in high magnetic field found a crossover in the behavior of the system appearing between 10 and 20 T for magnetic field perpendicular to the kagome planes ($\mathbf{H} \parallel \mathbf{c}$) and a gradual filling of the triplet band. It was proposed [12] that the strongest coupling ($J_1 = 234\text{ K}$) creates valence bonds between spin pairs and forms a “pinwheel” pattern around the regular kagome hexagon (inset to Fig. 1). The remaining three

couplings ($J_2 = 0.95J_1$, $J_3 = 0.85J_1$, $J_4 = 0.55J_1$) and an additional Dzyaloshinskii-Moriya (DM) interaction further define the energy structure of the system. A 12-site VBS state was shown to be energetically preferable to the 36-site VBS state proposed for the uniform kagome antiferromagnet. A later neutron scattering study [13] has indeed found evidence of a 12-site VBS ground state, separated from the first triplet state with a renormalized energy gap $\Delta(H=0) = \Delta(0) = 27\text{ K}$. Measurements in magnetic field up to 6 T, applied perpendicular to the kagome planes, show lifting of the triplet band degeneracy and a reduction of the singlet-triplet gap.

The availability of $\text{Rb}_2\text{Cu}_3\text{SnF}_{12}$ in the form of large single crystals has already stimulated fruitful experimental and theoretical work [11–15]. However, the microscopic properties of the 12-site “pinwheel” VBS ground state, as well as its behavior in high magnetic fields, are still unknown. In this Letter we report an NMR study of the on-site copper $^{63,65}\text{Cu}$ nuclei in magnetic fields up to 30 T, applied parallel to the c -axis. We find evidence of an unconventional magnetic lattice with strong staggered transverse magnetic moments. We determine the field dependence of the singlet-triplet gap, and show that there is no phase transition connected with the closing of the gap, but rather find a level anticrossing keeping the gap always open. Together with the field dependence of local spin polarizations, this points to a mixing of the singlet and the triplet states, typically associated with a DM interaction perpendicular to the field and/or a staggered g tensor component g_s . These properties provide a very stringent framework for a theoretical description of the ground state realized in $\text{Rb}_2\text{Cu}_3\text{SnF}_{12}$ compound.

When a single crystal sample is placed in a magnetic field, the NMR spectrum of the copper $^{63,65}\text{Cu}$ (spin $3/2$) nuclei will show 3 lines per isotope for each non-equivalent site: one central line surrounded by two satellites. This sextuplet of lines is multiplied by the number

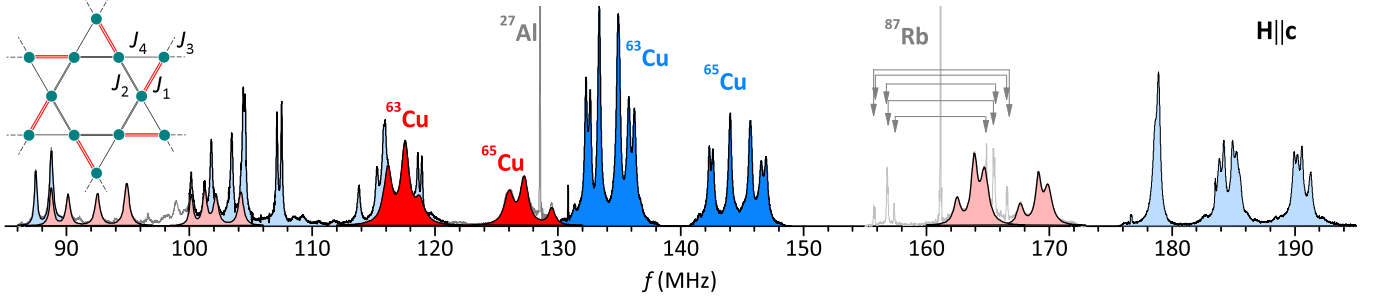


FIG. 1: (color online) $^{63,65}\text{Cu}$ spectrum of $\text{Rb}_2\text{Cu}_3\text{SnF}_{12}$ measured at 2.6 K and 11.568 T for the magnetic field parallel to the c-axis of the crystal. Colors and their hues are used to distinguish positively (red) and negatively (blue) polarized sites, as well as the central lines (dark color) and satellites (light color). Additional lines of ^{87}Rb and ^{27}Al (used for magnetic field calibration) are marked in grey. The inset shows the exchange couplings structure of a pinwheel cluster.

of inequivalent sites, e.g., the spectrum shown in Fig. 1 presents a very complicated structure spanning over 100 MHz, consisting of 72 NMR lines originating from 12 sites. To analyse such spectra, we follow closely the procedure and nomenclature used in Ref. [16]. For technical details see there the second column on page 2. The six NMR frequencies of each sextuplet of lines belonging to one copper site are determined by the quadrupolar coupling tensor, described by its principal component ν_Q and the asymmetry parameter η , by the Zeeman coupling to the local magnetic field H_{eff} , and by the (ϑ, φ) angles defining relative direction of that field with respect to the principal axes of the quadrupolar tensor. These 5 parameters are here further constrained by the known nuclear quadrupolar frequency $\nu_{NQR} = \nu_Q \sqrt{1 + \eta^2/3}$, as four different ν_{NQR} frequencies, all in the narrow range 49.8–55.3 MHz, have been reported in a previous study [17]. The main difficulty in the analysis of the spectra lies in the assignments of different sextuplets to lines in the NMR spectrum. This requires numerous trials and errors, where the correct assignment was recognized by successful fit to several complete spectra taken at different field values, leading to reasonable values of the fit parameters $(H_{\text{eff}}, \vartheta, \varphi, \nu_Q, \eta)_i$, where i denotes different Cu sites. In particular, for nearly all the sites we found $\vartheta \approx 24 \pm 2^\circ$, (while only two sites have somewhat smaller values $13 \pm 2^\circ$) which corresponds precisely to what is expected from the crystal structure [11]. That is, for all CuF_6 octahedra, the (average) planes passing through 4 tetragonally placed F^- ions that define the $d_{x^2-y^2}$ orbital of copper are tilted by 22° – 23° with respect to the kagome plane, see inset to Fig. 4.

Amongst the complete set of parameters, only the H_{eff} values are expected to be temperature (T) and field dependent. Once determined, the other parameters can be taken as constants, so that in the study of T - and H -dependence of spectra, from each NMR line position we can calculate the corresponding H_{eff} value. For these studies we have thus measured only the central lines of the spectra, meaning that each Cu site was represented

by two lines from two $^{65,63}\text{Cu}$ isotopes which should lead to the same H_{eff} value. As shown in Figs. 2(a) and 3(a) this is indeed the case. In these figures we have plotted the negative of the local field $-H_{\text{loc}} = H_0 - H_{\text{eff}}$, where H_0 is the applied field, which is directly proportional to the local spin polarization, $-H_{\text{loc}} = -\mathbf{A} \times 2 \langle \mathbf{S} \rangle - \mathbf{K}_{\text{orb}} \mathbf{H}_0$, up to relatively small constant correction due to the orbital contribution, estimated as $K_{\text{orb}} \approx 1.5\%$. Typical values of the hyperfine coupling tensor \mathbf{A} for the Cu nucleus in the CuF_6 environment are known [18], $A_{\parallel} \approx -18 \text{ T}$, $A_{\parallel}/A_{\perp} \approx 10$, where “ \parallel ” denotes the principal axis of the \mathbf{A} tensor, expected to be (nearly) parallel to the principal axis of the quadrupolar coupling tensor, defined by the angles (ϑ, φ) . In this case, both the longitudinal coupling constant $A_{zz} = A_{\parallel} \cos^2 \vartheta + A_{\perp} \sin^2 \vartheta$, as well as the transverse one $A_{z\perp} = \frac{1}{2}(A_{\parallel} - A_{\perp}) \sin 2\vartheta \cos \phi$ are known, and the measured $-H_{\text{loc}}$ directly reflects the corresponding local spin polarization (S_z, S_{\perp}, ϕ) , where ϕ denotes the azimuthal angle with respect to the direction of the ϑ tilt. It is clear that from one number, H_{loc} , one cannot *a priori* deduce three spin components. The necessary information to get S_z and S_{\perp} spin components is thus obtained from the analysis of the $-H_{\text{loc}}(T, H)$ dependence (Figs. 2 and 3).

Our NMR spectrum shown in Fig. 1 reveals a large number of lines, corresponding to many different local fields originating from crystallographically and/or magnetically different sites. In contrast to that, the room temperature crystal structure predicts only *two* inequivalent copper sites in the unit cell. In order to understand the origin of the observed distribution of local fields, we have tracked their temperature dependence, shown in Fig. 2(a). There, one can resolve two families of sites (marked with A (green) and B (orange)) occupied in the ratio $P(A):P(B) = 8:4 = 2:1$, which can be associated with 12 sites per unit cell of the crystal structure below 215 K. That is, close to this temperature a small structural distortion has been observed by X-ray scattering [13], leading to the enlargement of the lattice cell to $2a \times 2a$, but the superlattice peaks were too weak to fully

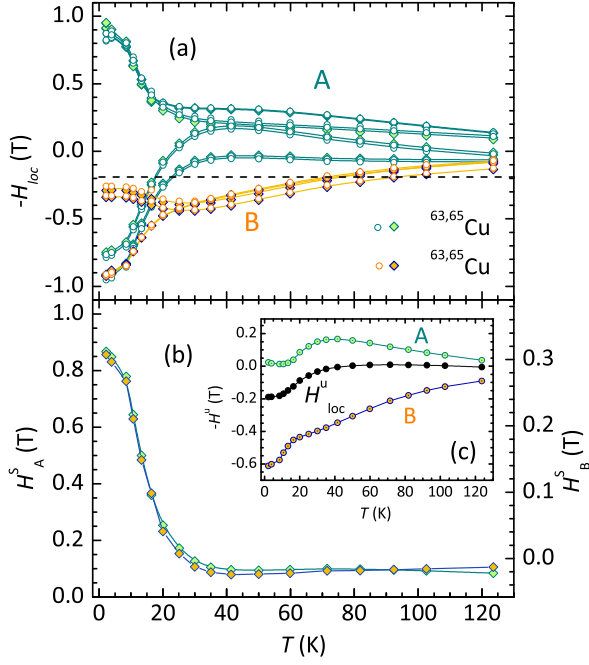


FIG. 2: (color online) (a) Temperature dependence of the local fields at 13.0 T. Two groups of sites are marked by the green (A) and orange (B) symbols. Empty (filled) symbols show the values obtained for ^{63}Cu (^{65}Cu) isotope. The dashed line marks estimated orbital contribution ($K_{\text{orb}} \approx 1.5\%$). (b) The average local *staggered* field at sites A (green, left scale) and B (orange, right scale). (c) The *uniform* hyperfine field averaged over the A, B and all sites (green, orange and black circles, respectively).

resolve the new structure at lower temperature. While this structural transition was not detected in dc susceptibility, such subtle deformations can cause the splitting of the NMR lines. Furthermore, in Fig. 2(a) it is easy to observe the local “pairs” of each family that develop opposite polarizations at low temperature, defining thus the local staggered ($H_{A,B}^s$) and uniform ($H_{A,B}^u$) fields,

$$\begin{aligned} H_{A,B}^s &= (\langle H_{i+} \rangle_{A,B} - \langle H_{i-} \rangle_{A,B})/2, \\ H_{A,B}^u &= (\langle H_{i+} \rangle_{A,B} + \langle H_{i-} \rangle_{A,B})/2, \end{aligned} \quad (1)$$

where the average is taken over the upper (H_{i+}) or lower (H_{i-}) local fields of either A or B family of lines. In Fig. 2(b) we can see that both A and B sites develop very strong staggered moments below 30 K ($\approx \Delta(0)$). Additionally (see Fig. 2(c)), the two families of lines also develop distinct positive (H_A^u) and negative (H_B^u) uniform magnetizations. When the temperature is raised, the distribution of the local fields is reduced but retains a finite value, even at 120 K ($\approx 4\Delta(0)$) [19]. This site-inequivalence is attributed to the previously mentioned structural distortion of the lattice [13]. On the other hand, the development of the staggered (H_{loc}^s) and uniform (H_{loc}^u) fields at temperatures below the zero field gap in Fig. 2(b) is clearly related to the formation of the

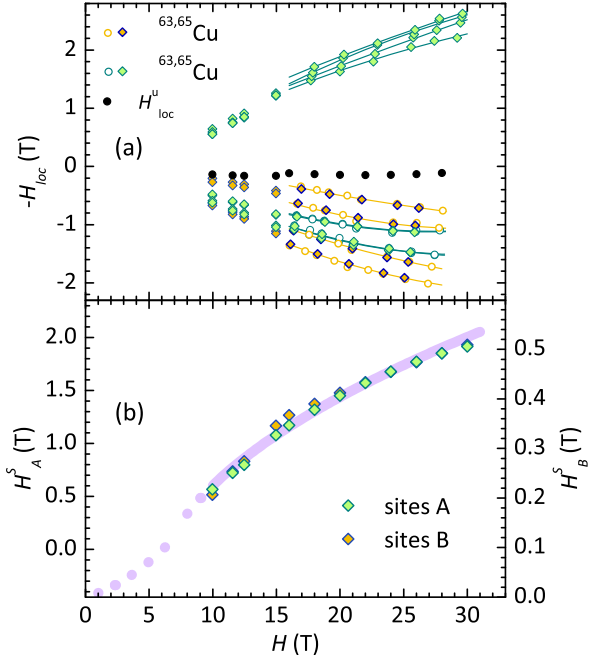


FIG. 3: (color online) (a) Magnetic field dependence of the local fields, with the same symbol and color code as in Fig. 2. (b) The average local staggered field. The thick line is a guide for the eye showing a square root dependence, while the dotted line shows an expected qualitative behavior for lower magnetic fields.

local spin order.

As already mentioned, both transverse and longitudinal magnetization contribute to H_{loc} , and, due to the uncertainty in the site environments and the complexity of the spectra, we could not find a way to formally separate the two contributions. However, considering their relative size at low temperature, $|H^s| \gg |H^u|$, it is natural to associate the staggered (uniform) fields $H^{s(u)}$ defined by Eqs. (1) to the transverse (longitudinal) local spin polarization S_{\perp} (S_z), respectively. This is further supported by the field dependence of these values and the physics behind, as discussed later. Within this attribution we find very big low- T values for the local transverse staggered spin polarization, $S_{\perp} \cos \phi \approx 14\%$ and 6% for the A and B sites respectively, while the local uniform fields correspond to much smaller spin polarization of $S_z \approx 1.2\%$ and -2% . While in this way only a projection $S_{\perp} \cos \phi$ is determined, in all cases the spins polarizations lie nearly completely in the kagome plane, $S_{\perp} \gg |S_z|$.

We observe that the total average $\langle S_z \rangle$ component is almost fully cancelled out, $P(A) \langle S_z \rangle_A + P(B) \langle S_z \rangle_B \approx 0$, but the true value cannot be precisely defined, because of the uncertainty in the estimate of the orbital shift K_{orb} defining the zero. As regards the transverse staggered components, the smaller value of H_B^s for sites B can be explained either as a weaker polarized moments having equivalent orientations, $\phi_A \approx \phi_B$, or moments of similar

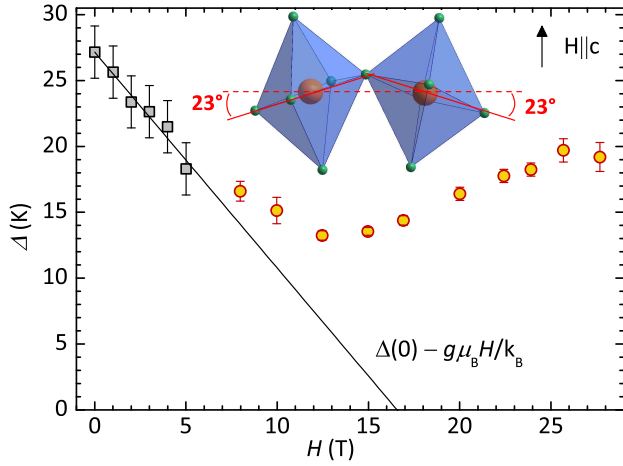


FIG. 4: (color online) Magnetic field dependence of the singlet-triplet energy gap measured by T_1^{-1} (red-yellow circles) and by neutron scattering (black-grey squares, from Ref. [13]). The inset shows neighboring CuF_6 octahedra.

size but different ϕ values, e.g., $\phi_A \approx 0$ and $\phi_B \approx 65^\circ$. We cannot differentiate between these two cases, but general image of large staggered magnetization within the kagome planes is not affected by this uncertainty.

We have also followed the magnetic field dependence of the local polarizations up to 30 T (Fig. 3), measured at 3.9 K where the temperature dependence of the spin polarizations saturates. The field dependence of $H_{A,B}^s$ (Fig. 3(b)) is clearly different from the high field magnetization [11] and follows approximately a square-root dependence, reaching at 30 T a polarization of $S_\perp \cos \phi \approx 30\%$ for the A sites. Similar temperature and magnetic field dependence of local moments was found [20] in $\text{SrCu}_2(\text{BO}_3)_2$, another 2D frustrated dimer system. There, a moderate in-plane DM interaction ($D/J = 0.034$) was enough to mix the singlet and triplet states and thus create considerable transverse staggered moments, while the longitudinal moments remain much smaller. In $\text{Rb}_2\text{Cu}_3\text{SnF}_{12}$, the DM interaction is estimated to be much stronger ($D/J = 0.18 - 0.2$), but only the longitudinal c-axis component of the \mathbf{D} vector has been considered so far. Our results imply that a significant component *parallel* to the kagome plane should also be taken into consideration.

While the application of the critical field in spin-dimer systems is expected to close the singlet-triplet gap by the level-crossing, leading to a new, polarized phase, mixing of the singlet and triplet states will keep the gap open (“anti-crossing”). In order to follow the magnetic field dependence of this gap, we have performed the measurements of the nuclear spin-lattice relaxation rate T_1^{-1} which probes the dynamics of the low-energy excitations. Importantly, no qualitative changes in the spectra nor any T_1^{-1} anomaly were observed down to 1.5 K, evidenc-

ing the absence of a phase transition. For a fixed field, the temperature dependence of T_1^{-1} below 6 K shows an activated behavior, $\propto e^{-\Delta(H)/T}$, typical of a 2-magnon process, allowing us to determine the value of the gap, $\Delta(H)$. All central NMR lines follow the same temperature dependence, meaning that the gap opens homogeneously in the system. As the field is raised from 8 T to 13 T, the gap value is seen to decrease (Fig. 4), and the NMR data smoothly continue those determined from the neutron-scattering up to 6 T [13]. Close to 13 T the gap value passes through a broad minimum after which it again increases at higher fields. The residual value of the gap $\Delta(13 \text{ T}) \approx \Delta(0)/2$ is large, which is a clear evidence for important antisymmetric exchange interactions [21], inducing the anticrossing of singlet and triplet energy bands. The anticrossing gap associated to the staggered g tensor component g_s (due to tilting of the CuF_6 octahedra by $\vartheta \approx 23^\circ$), or to a strong transverse component of the DM vector in systems of *weakly* coupled dimers is expected to be much smaller. Remembering that the zero-field gap value in $\text{Rb}_2\text{Cu}_3\text{SnF}_{12}$ is renormalized to $\Delta(0) \approx \langle J \rangle / 7$ by frustrating competing interactions, we conclude that the corresponding renormalization of the residual gap must be weaker.

Recently, it has been found that a strong DM interaction can drive the ground state [22] of the spin-1/2 kagome antiferromagnet from frustration dominated spin-liquid to a Néel ordered phase. Indications of such a state have been found in herbertsmithite [23], where slowing down of spin fluctuations acquires a $\sqrt{H - H_c}$ dependence on magnetic field, accompanied with the broadening of the width of the powder spectrum. Similarly, a distribution of the local hyperfine fields and freezing of spin fluctuations have been detected in volborthite [24]. There, the interplay of strong DM interaction and a non-uniform Heisenberg coupling is proposed [25] to result with an exotic coexistence of dimer and Néel states. It is therefore reasonable to expect that in $\text{Rb}_2\text{Cu}_3\text{SnF}_{12}$ a similar combination of multiple Heisenberg couplings and a strong antisymmetric interaction will bring about some quasi-Néel state of strongly interacting dimers, characterized by staggered magnetization.

In summary, by the on-site $^{63,65}\text{Cu}$ NMR of the “pin-wheel” kagome compound $\text{Rb}_2\text{Cu}_3\text{SnF}_{12}$ we reveal microscopic details of the ground state of this system, allowing for direct testing of theoretical models. In the field perpendicular to the kagome planes and at low temperature the NMR spectra evidence a strong staggered transverse (i.e. in-plane) spin polarization, growing approximately as a square-root of magnetic field. The field dependence of the singlet-triplet gap measured via the T_1^{-1} data presents an anticrossing of the energy levels with a large residual gap value $\Delta(13 \text{ T}) \approx \Delta(0)/2$. These findings point to the mixing of the singlet and triplet levels, typically associated with a transverse component of the Dzyaloshinskii-Moriya interaction and a staggered g

tensor, which has not yet been studied theoretically in the environment of strong frustration of kagome type.

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